

# Enhanced Lithiation of Doped 6H Silicon Carbide (0001) via High Temperature Vacuum Growth of Epitaxial Graphene

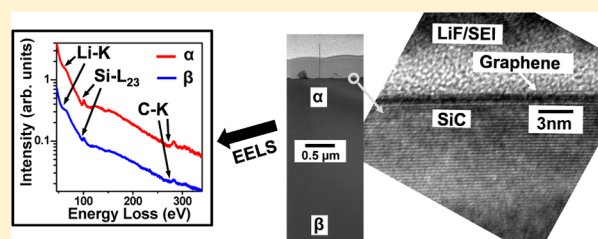
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## S Supporting Information

**ABSTRACT:** The electrochemical lithiation capacity of 6H silicon carbide (0001) is found to increase by over 1 order of magnitude following graphitization at 1350 °C in ultrahigh vacuum. Through several control experiments, this Li-ion capacity enhancement is correlated with SiC substrate doping and removal of the native oxide surface layer by thermal annealing, which renders both the bulk and surface electrically conductive. Characterization via multiple depth-resolved spectroscopies shows that lithium penetrates the activated SiC upon lithiation, the bulk lattice spacing does not appreciably change, and the surface structure remains largely intact. The electron energy-loss spectroscopy (EELS) extracted compositional ratio of Li to Si is approximately 1:1, which indicates an intrinsic bulk Li capacity in activated SiC of 670 mAh g<sup>-1</sup>. In addition, inelastic X-ray scattering spectra show changes in the Si chemical bonding configuration due to lithiation. X-ray scattering data show a decrease in the SiC Bragg peak intensity during lithiation, suggesting changes to the bulk crystallinity, whereas the emergence of a diffuse scattering feature suggests that lithiation is associated with the development of substrate defects. Overall, these results illustrate that the electrochemical capacity of a traditionally inert refractory material can be increased substantially via surface modification, thus suggesting a new strategy for improving the performance of next generation Li-ion battery electrodes.



## 1. INTRODUCTION

The increased use of rechargeable batteries for portable electronics and electric vehicles motivates the need for smaller, lighter, safer, and more durable batteries.<sup>1</sup> The capacity of a Li-ion battery is determined largely by its electrode materials, which are currently graphite for the anode and a lithium-metal-oxide (LiMO<sub>2</sub>, M = Co, Ni, and Mn) or lithium-metal-phosphate (e.g., LiFePO<sub>4</sub>) for the cathode.<sup>2,3</sup> Among the many promising replacements for the anode, silicon has the highest theoretical capacity (4009 mAh/g), which corresponds to the maximum uptake of 21 Li per 5 Si atoms.<sup>4</sup> However, silicon suffers from a large volumetric expansion of up to 300% and amorphization during lithiation,<sup>5</sup> which introduces challenges for its use as a stable battery anode upon repeated cycling.<sup>6–9</sup>

Another important factor for battery performance is the structure and composition of the solid electrolyte interphase (SEI) formed on the electrodes. In the case of graphite, the SEI layer helps protect the electrode and electrolyte from degradation, but also can be deleterious by impeding lithiation processes.<sup>5,10</sup> Methods have been proposed to create an artificial SEI by depositing thin films of lithium-ion conducting

materials, leading to modest improvements in capacity and increases in battery lifetime.<sup>11–17</sup>

Composite materials hold promise for next generation Li-ion battery anodes. In particular, silicon-carbon composites are now commonly explored as anode materials because the Si component can provide a significantly enhanced capacity and the C component can act simultaneously as an active electrode and an electronic bridge between the particles.<sup>18–26</sup> Architectures of Si and C that concurrently provide high capacity and long lifetime are therefore of great interest to the lithium battery community.<sup>27</sup> On the other hand, silicon carbide (SiC) is an inert refractory material that is not traditionally viewed as a promising candidate for Li-ion battery electrodes.<sup>28</sup> For example, SiC has been identified as the inactive matrix in Si-SiC “active-inactive” composite anodes in previous Li-ion battery studies.<sup>29</sup>

In recent years, 6H-SiC (space group *P6<sub>3</sub>mc*) has received increased interest as a substrate for epitaxial growth of graphene.<sup>30–33</sup> In particular, it has been found that high

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temperature annealing of SiC(0001) leads to the formation of epitaxial graphene at the surface (EG/SiC) with low defect density and superlative performance in high frequency electronic devices.<sup>30,31</sup> The interface between epitaxial graphene and the underlying SiC substrate is carbon-rich and possesses a surface reconstruction designated as  $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ .<sup>34–36</sup> Recent studies of epitaxial graphene on SiC, where Li was vapor deposited on the surface, have shown evidence for Li diffusion through graphene into the subsurface  $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$  region leading to Li–Si bonding.<sup>37</sup> It has also been shown that Li can be ion implanted into SiC interstitial sites,<sup>38</sup> and the Li diffusion constants have been measured.<sup>39</sup> These studies suggest that it may be possible to electrochemically lithiate SiC when activated.

Herein, we report substantial enhancement of the electrochemical lithiation capacity of traditionally inert SiC via surface graphitization. This unexpected observation led us to perform a broad series of measurements to characterize the process by which lithiation occurs in this system and the associated changes in the electrode structure. Specifically, the effects of various high temperature treatments and substrate doping on the electrochemical lithiation of SiC are delineated, demonstrating that thermal processing can lead to significantly enhanced Li-ion capacity. Depth-resolved spectroscopic studies and cross-sectional imaging are then presented, which indicate that Li penetrates into the bulk structure. Through synchrotron X-ray analysis, the surface structure is found to be preserved following lithiation, and the lattice parameter of the underlying activated SiC structure is not substantially altered, although changes to crystallinity are observed. This extensive characterization corroborates the electrochemical lithiation data and confirms the critical role that surface treatments can play in determining the Li-ion capacity of battery electrodes.

## 2. EXPERIMENTAL SECTION

6H-SiC single crystal wafers of approximately 250  $\mu\text{m}$  thickness and doped n-type by nitrogen to a resistivity between 0.02 and 0.2  $\Omega\text{ cm}$  were purchased from CREE. The area of the samples was measured using digital calipers with an error of 3%. Samples were sonicated in acetone and isopropanol before use, and samples in this condition are termed “as-received”.

EG/SiC samples were produced in a UHV chamber with a base pressure below  $1 \times 10^{-10}$  Torr unless otherwise noted. The SiC was resistively heated by passing current through the SiC while temperatures were monitored using an optical pyrometer (Cyclops) at an emissivity of 0.85. The SiC was degassed overnight at 600  $^\circ\text{C}$  and then annealed for 2 min at 1000  $^\circ\text{C}$ . The SiC was then flashed 3 times at 1100  $^\circ\text{C}$  for 2 min each. After each flash, the sample was allowed to cool for 10 min. Lastly, the SiC was graphitized at 1300  $^\circ\text{C}$  for 2 flashes and then 10 flashes at 1350  $^\circ\text{C}$  for 1 min apiece.

The SiC with  $\sqrt{3} \times \sqrt{3}$  reconstruction was prepared in UHV by first degassing at 600  $^\circ\text{C}$  overnight and then annealed for 2 min at 1000  $^\circ\text{C}$ . It was then flashed at 1100  $^\circ\text{C}$  for 5 min. The furnace annealed sample was annealed by ramping to 1100 at 5  $^\circ\text{C min}^{-1}$  and then immediately cooled at 5  $^\circ\text{C min}^{-1}$  in an alumina tube under a flow of 99.999% argon gas at atmospheric pressure. The polished EG/SiC sample was polished using diamond lapping paste with 0 to 0.5  $\mu\text{m}$  particle size (McMaster Carr). Atomic force microscopy topography imaging showed that the graphene structure was removed and that the polishing introduced some additional scratches into the surface. The undoped EG/SiC sample was first

hydrogen etched and then graphitized at 1620  $^\circ\text{C}$  for 2 h in an argon atmosphere at 100 mbar.

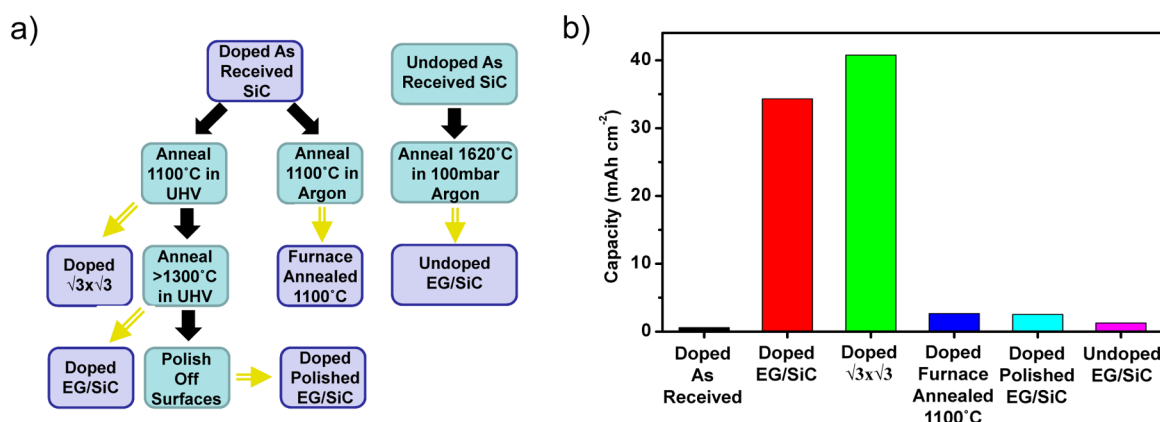
Electrochemical lithiation and delithiation was performed using two-electrode beaker type cells with Li metal as the counter electrode. The electrolyte used was 1 M  $\text{LiPF}_6$  (99.99%, Sigma Aldrich) in 1:1 by volume ethylene carbonate to dimethyl carbonate (Anhydrous, Sigma Aldrich). Galvanostatic charging was performed using a current source (Keithley 220) set to 10  $\mu\text{A}$ , and a multimeter was used to measure voltage (Keithley 2001 or 2002) versus Li metal. First lithiation capacity was found by lithiating the sample to 0 V repeatedly until the open circuit voltage was under 0.5 V after 8 h.

Transmission electron microscopy (TEM) samples were prepared by standard FIB lift-out preparation methods using a Helios NanoLab dual beam FIB/SEM (FEI) unless otherwise noted.<sup>40</sup> TEM images and electron energy loss spectroscopy (EELS) spectra were taken on a JEM-2100F TEM (JEOL) at 200 kV. EELS (in combination with scanning transmission electron microscopy, STEM with 1 nm spot size) was performed using a post column Gatan imaging filter fitted to the field emission JEOL TEM. The spectra were obtained with a spectrometer dispersion of 0.5 eV/channel. Quantitative elemental analysis was performed using Gatan Digital Micrograph software with background subtraction and corrections for plural scattering.

Inelastic X-ray scattering (IXS) was performed at sector 20ID-B at the Advanced Photon Source (APS) at Argonne National Laboratory.<sup>41</sup> The energy loss was scanned by adjusting the incident energy with a two crystal Si (111) monochromator while keeping the scattered energy fixed such that each Si analyzer is at the (555) Bragg condition ( $E_2 = 9891$  eV). Quasielastic scattering was used to calibrate the energy loss and determine the overall resolution (1.3 eV). Data were collected at incident angles of 0.6 $^\circ$ , 1.3 $^\circ$ , 2 $^\circ$ , and 11 $^\circ$ , which have 1/e penetration depths of 0.5, 1.1, 1.6, and 8.5  $\mu\text{m}$  into SiC, respectively.

Focused ion beam (FIB) and scanning electron microscopy (SEM) were taken using the Helios NanoLab dual beam FIB/SEM (FEI). It should be noted that the SEM images are taken at a 52 $^\circ$  to the surface of the cross-section giving a view of both the top surface of the sample as well as the cross-section. Secondary ion mass spectrometry (SIMS) depth profiling was performed with a time-of-flight SIMS Trift-III system (Physical Instruments) using a 5 kV Ga pulsed sputtering system. The sputtered region was 100  $\mu\text{m} \times 100 \mu\text{m}$  and the region analyzed was 25  $\mu\text{m} \times 25 \mu\text{m}$  to minimize redeposition from the edges into the analyzed region.

In situ X-ray reflectivity measurements were performed at sector SID-C and 33ID-D at the APS at Argonne National Laboratory using 17.00 keV X-rays with a beam size of 1.0 mm horizontally and 0.1 mm at SID-C and 0.3 mm at 33ID-D vertically. Scattered X-rays were detected using an X-ray CCD area detector (Princeton Instruments 7501-0002). Reflectivity of the SiC Bragg peak was also measured using a point detector (Cyberstar) with a beam size of 0.05 mm vertically and 1 mm horizontally. Samples were contained in a custom-made electrochemical cell with a 7  $\mu\text{m}$  thick Kapton window. The reflectivity data, extracted from the CCD 2D pixel maps,<sup>42</sup> were least-squares fitted with a crystal truncation rod (CTR) formalism<sup>43</sup> for a parametrized model of the electron density profile shown in Figure 6b.



**Figure 1.** (a) Flowchart showing the various processing steps to achieve the different samples shown in panel b. The doped SiC is doped n-type with nitrogen to a resistivity of 0.044  $\Omega$  cm. (b) Comparison of the first cycle lithiation capacity for a variety of 6H-SiC (0001) single crystal samples.

### 3. ELECTROCHEMICAL LITHIATION

A nitrogen-doped, as-received sample of 6H-SiC (0001), that has not undergone thermal treatments and therefore possesses a native oxide layer, was used as a baseline for SiC lithiation studies. This sample has a sheet resistance in excess of 10  $M\Omega$   $\square^{-1}$ . The first lithiation capacity (as defined in the Experimental Section) was 0.6 mAh cm<sup>-2</sup> as shown in comparison with other SiC samples in Figure 1. This small apparent capacity can primarily be attributed to SEI formation due to reaction with the electrolyte at electrochemical potentials below  $\sim 1.5$  V vs Li<sup>0</sup>.

A sample of EG/SiC was prepared by graphitization of a doped SiC sample in ultrahigh vacuum (UHV) ("doped EG/SiC") to form a mix of single and bilayer graphene with small portions of the ( $6\sqrt{3} \times 6\sqrt{3}$ )R30° reconstruction exposed on the Si-face. The sheet resistance of this sample was 0.2  $\Omega$   $\square^{-1}$  (i.e., almost 8 orders of magnitude lower than the as-received sample). This sample has a first lithiation capacity of 34 mAh cm<sup>-2</sup>, which is approximately 50 times greater than the doped as-received sample. It should be noted that several EG/SiC samples were successfully lithiated to more than 1 order of magnitude greater capacity than as-received SiC, thus verifying the reproducibility of this observation. This enhanced lithium insertion capacity could be due to a combination of factors such as surface conductivity, bulk doping, and defects induced during thermal processing. To understand how each of these factors contribute to the increased lithiation capacity, we investigated SiC samples with various dopant levels and surface structures.

To test if the graphene layers play a crucial role in the lithiation process, a doped sample was annealed in UHV to attain the  $\sqrt{3} \times \sqrt{3}$  surface reconstruction. This structure precedes the formation of the ( $6\sqrt{3} \times 6\sqrt{3}$ )R30°, and therefore no graphene layers are formed on this surface. This sample was then placed into an inert atmosphere to minimize surface oxidation before lithiation, thereby maintaining sheet resistance on the order of the graphitized sample. The first lithiation capacity of this  $\sqrt{3} \times \sqrt{3}$  sample is similar to that of the fully graphitized sample (41 mAh cm<sup>-2</sup>), which indicates that the graphene itself does not play a critical role in SiC lithiation. It should however be noted that this reconstruction degrades (i.e., oxidizes) in air while graphitized samples are exceptionally inert, presenting clear practical advantages for EG/SiC.

To determine whether the lithiation capacity is caused only by heating the bulk SiC, a doped sample was heat treated to

1100 °C (the same temperature used to form the  $\sqrt{3} \times \sqrt{3}$  reconstruction in UHV) in a flow of argon at atmospheric pressure. The increased pressure reduces the evaporation rate of Si and O, thereby inhibiting the formation of the  $\sqrt{3} \times \sqrt{3}$  reconstruction and removal of the surface oxide. This sample possesses a sheet resistance greater than 10  $M\Omega$   $\square^{-1}$ . The capacity of this sample was 2.7 mAh cm<sup>-2</sup>, which is greater than that of the as-received sample but is still an order of magnitude smaller than the graphitized or  $\sqrt{3} \times \sqrt{3}$  samples. This intermediate lithiation capacity may be due to changes in the native oxide thickness or other effects of the heat treatment.

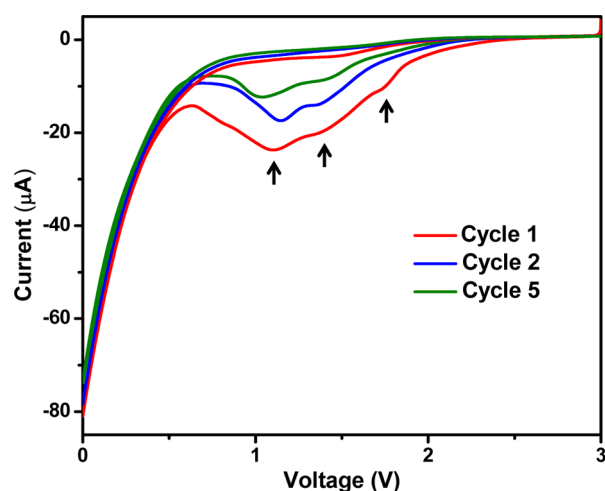
To further show that the surface oxide removal is a critical factor in SiC lithiation, a UHV graphitized sample (prepared identically as the doped EG/SiC sample) was mechanically polished with diamond lapping paste to expose the bare SiC crystal. During and after polishing the native oxide reforms on the SiC surface giving a sheet resistance in excess of 10  $M\Omega$   $\square^{-1}$ . The capacity of this sample was 2.5 mAh cm<sup>-2</sup>, similar to the heat treated sample.

The effects of substrate doping can be elucidated through the use of an undoped (semi-insulating) EG/SiC sample as a comparison to the doped case. After graphitization by furnace annealing, the surface is almost completely covered with monolayer graphene, leading to a sheet resistance on the Si-face of 5 k $\Omega$   $\square^{-1}$ . This value is substantially higher than the doped EG/SiC sample since the SiC does not contribute significantly to the conductivity. The lithiation capacity of this undoped EG/SiC sample was 1.3 mAh cm<sup>-2</sup>, illustrating the importance of substrate doping in the lithiation of SiC.

These experiments define the various factors that are necessary to enhance the lithiation capacity of SiC. Substrate doping is clearly important as it increases the electrical conductivity of the bulk SiC, thus enabling the electron transfer needed for electrochemistry. Doping may also play a role by lowering the insertion energy for Li in SiC,<sup>44</sup> although it is difficult to deconvolute this factor experimentally from that of increased conductivity. In addition, removal of the native oxide from the SiC surface is critical, presumably because it enables improved surface electrical conductivity. The removal of the native oxide also eliminates the need for Li diffusion through that barrier coating. High temperature annealing may also introduce defects in the surface and/or bulk of SiC that promote Li diffusion.

Cyclic voltammetry (CV) yields additional information about the voltages at which various electrochemical reactions occur.

There are three peaks that occur at approximately 1.8, 1.4, and 1.0 V (indicated by arrows in Figure 2) during the negative



**Figure 2.** Cyclic voltammetry of a graphitized n-type doped SiC wafer between 0 and 3 V at a rate of  $10 \mu\text{V s}^{-1}$ .

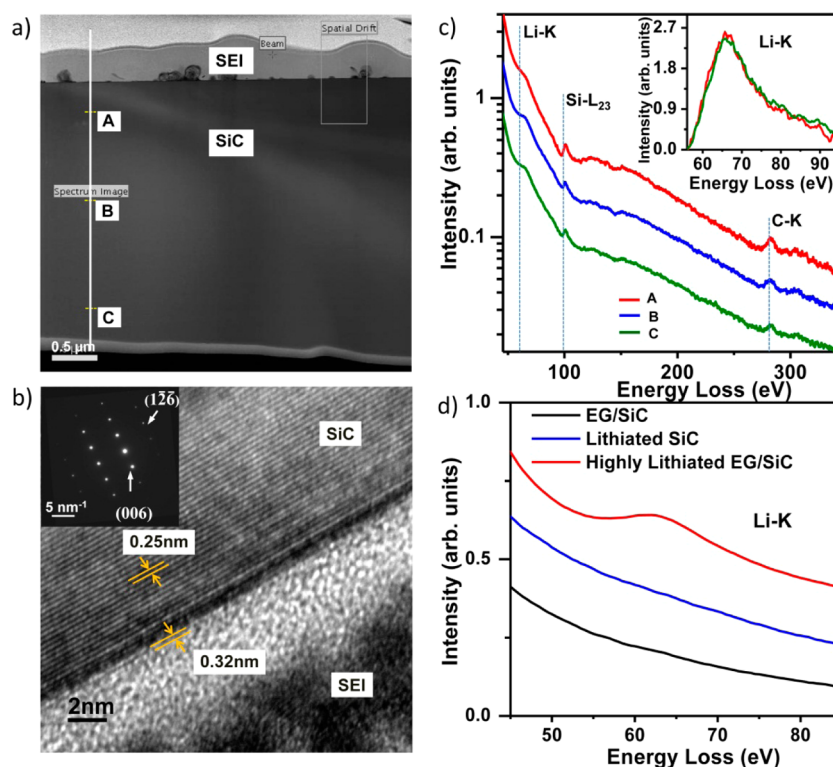
direction sweep of cycle 1. In later cycles, only the 2 lower voltage peaks appear indicating likely changes between the initial solid electrolyte interphase (SEI) formation and relithiation processes. We speculate from the CV data that, at low voltages (0–0.5 V), further irreversible breakdown of the electrolyte and possible lithiation of the SiC occurs, and that the latter process is largely irreversible (see the Supporting

Information, Figure S2, for lithiation and delithiation curves). To gain further insight into the lithiation process, extensive characterization of lithiated EG/SiC is presented below.

## 4. SPECTROSCOPY AND CROSS-SECTIONAL IMAGING

**4.1. Transmission Electron Microscopy and Electron Energy Loss Spectroscopy.** Direct observation of the spatial location of Li in the lithiated SiC crystal below the EG/SiC (0001) interface was achieved by cross-sectional transmission electron microscopy (TEM) in combination with electron energy loss spectroscopy (EELS). These samples were prepared by focused ion beam (FIB) lift-out methods. In particular, a Pt beam induced deposited (BID) protective layer was created on top of the SEI layer to avoid surface damage during the FIB preparation process. The resulting images and spectra are summarized in Figure 3. A low magnification cross-sectional TEM image of an EG/SiC sample (Si-face) lithiated to  $\sim 14 \text{ mAh cm}^{-2}$  is shown in Figure 3a (the C-face SiC (0001) data is shown in the Supporting Information, Figure S4). In this image, an approximately  $0.5 \mu\text{m}$  SEI layer and the Pt BID layer are clearly resolved above the EG/SiC surface.

Figure 3b shows a representative high resolution TEM (HRTEM) image of the same sample near the SEI/SiC interface, observed along the  $[21\bar{2}0]$  direction. The SiC (0001) crystal lattice structure is clearly observed in this sample. The selected area diffraction (SAD) pattern, using a  $10 \mu\text{m}$  SAD aperture (shown as an inset), further indicates that the SiC structure remains intact following lithiation. The HRTEM image shows a  $0.32 \text{ nm}$  spacing in between the SiC crystalline region and SEI, which indicates a single layer of graphene.



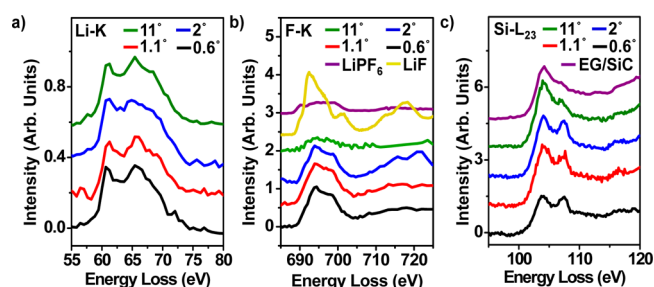
**Figure 3.** TEM micrographs and EELS spectra for a highly lithiated ( $14 \text{ mAh cm}^{-2}$ ) graphitized SiC (EG/SiC) sample (Si-face). (a) Cross-section of the sample. (b) Cross-sectional HRTEM image observed along the  $[21\bar{2}0]$  direction of 6H-SiC near the SiC/SEI interface (inset shows the selected area diffraction (SAD) pattern from SiC). (c) EELS spectra from different depths of the sample indicated by A, B, and C in (a) (inset: EELS background subtracted spectra for Li-K edge from approximately  $0.4 \mu\text{m}$  (A) and  $2.6 \mu\text{m}$  (C) within the SiC region). (d) Comparison of Li-K edge of highly lithiated EG/SiC with as-received SiC (lithiated to 0 V) and non lithiated EG/SiC at  $\sim 0.8 \mu\text{m}$  depth.

To probe the Li depth profile within the SiC, EELS measurements were performed. The EELS results of Figure 3c are representative spectra taken along the line shown in Figure 3a (near points A, B, and C) having depths of approximately 0.4, 1.4, and 2.6  $\mu\text{m}$  below the SiC surface, respectively. The EELS spectra have Li, Si, and C signals in the bulk SiC region at all depths measured. Background corrected Li–K edge<sup>45,46</sup> from approximately 0.4 and 2.6  $\mu\text{m}$  inside the SiC crystalline region are shown in the inset of Figure 3c. These spectra show significant Li concentration in the crystalline SiC even at a depth of 2.6  $\mu\text{m}$ . Furthermore, the Li K-edge position indicates that the Li is not metallic.<sup>47</sup> Quantification of the relative Si and Li EELS signals show that the Li to Si atomic concentration ratio is approximately  $\{1 \pm 0.2\}:1$  (see the Supporting Information for quantification methodology in Section S6 and depth dependence in Figure S5). A 1:1 Li to Si ratio indicates a maximum capacity of 670 mAh  $\text{g}^{-1}$ , which is approximately double that of graphite.

To address the possibility that the TEM/EELS preparation methods transported Li from the SEI into the bulk, we prepared a lithiated (18 mAh  $\text{cm}^{-2}$ ) EG/SiC sample using traditional cross-sectional TEM sample preparation methodology (methodology discussed in detail in the Supporting Information section S7).<sup>48</sup> The sample prepared by this second method also shows a similar Li concentration ( $\{0.72 \pm 0.1\}:1$  Li to Si) inside the bulk SiC.

For comparison purposes, cross-sectional TEM and EELS data were also taken for lithiated as-received SiC (galvanostatically driven to 0 V) and nonlithiated EG/SiC samples (with traditional TEM preparation protocols). The SiC (0001) crystal structure is clearly observed in the HRTEM images for both samples (see the Supporting Information for nonlithiated EG/SiC, Figure S6). EELS Li–K edge spectra for lithiated and nonlithiated EG/SiC along with lithiated as-received SiC at  $\sim 0.8 \mu\text{m}$  depth are shown in Figure 3d. In contrast to the lithiated EG/SiC, EELS data for lithiated as-received SiC show no evidence of the Li K-edge signal at  $\sim 0.8 \mu\text{m}$  depth (see the Supporting Information, Figure S7). These results are consistent with the observed Li capacity of the systems.

**4.2. Inelastic X-ray Scattering.** We used inelastic X-ray scattering (IXS) to gain more evidence for the distribution of lithium in the 14 mAh  $\text{cm}^{-2}$  lithiated EG/SiC. IXS provides spectroscopic information that is similar to EELS but due to the high-penetrating-power of hard X-rays does not require vacuum or elaborate sample processing. The relative IXS signal is proportional to the overall stoichiometry of the sample.<sup>49,50</sup> IXS probes the distribution of an element at or below an interface by controlling the penetration depth of the X-ray beam into the sample by changing the angle of incidence. IXS spectra for Li, F, and Si were collected at incident angles of  $0.6^\circ$ ,  $1.3^\circ$ ,  $2^\circ$ , and  $11^\circ$  with respect to the surface plane, which have  $1/e$  penetration depths in SiC of approximately 0.5, 1.1, 1.6, and 8.5  $\mu\text{m}$ , respectively. The results are shown in Figure 4. The IXS spectrum of the Li K-edge (Figure 4a) does not change substantially with incident angle. This observation indicates that the Li distribution extends in excess of the largest probe depth (8.5  $\mu\text{m}$ ). In contrast, the F K-edge spectra (Figure 4b) is unlike that of Li and shows a significant decrease in signal at  $11^\circ$  confirming that fluorine is only present at the surface (i.e., in the SEI). The F K-edge spectra appear to be a combination of LiF and residual  $\text{LiPF}_6$  salt. The Si  $L_{23}$ -edge spectra (Figure 4c) show a reduced Si signal at  $0.6^\circ$  due to attenuation of the X-ray beam through the surface SEI layer. Note that the IXS



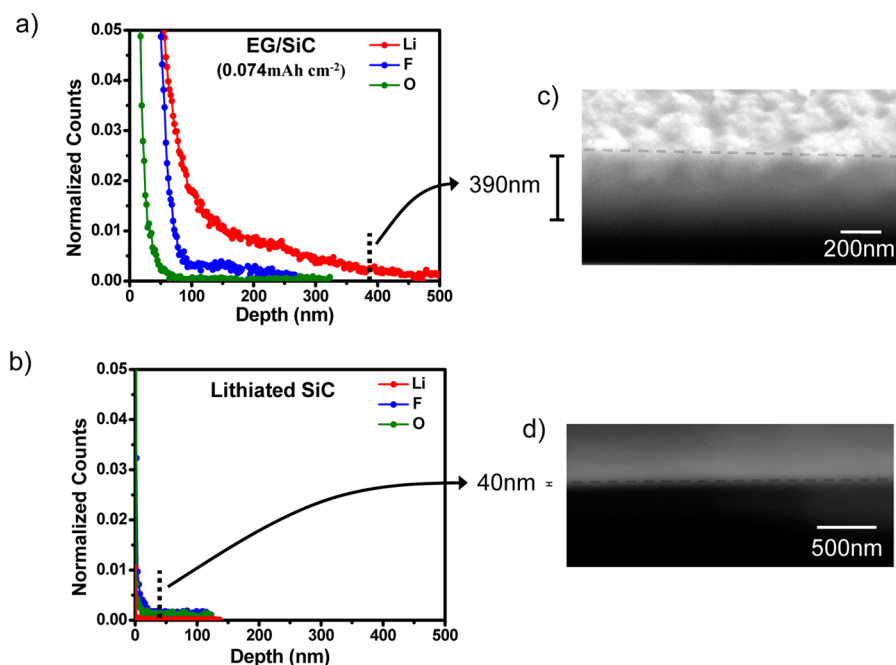
**Figure 4.** IXS data of the 14 mAh  $\text{cm}^{-2}$  lithiated EG/SiC sample (offset vertically for clarity) for the (a) Li K-edge, (b) F K-edge with reference spectra of LiF and  $\text{LiPF}_6$ , and (c) Si  $L_{23}$ -edge with a nonlithiated EG/SiC sample as a reference. Data were obtained at sample angles of  $0.6^\circ$ ,  $1.1^\circ$ ,  $2^\circ$ , and  $11^\circ$  to the incident X-ray beam. These angles correspond to  $1/e$  penetration depths in SiC of 0.5, 1.1, 1.6, and 8.5  $\mu\text{m}$ , respectively.

spectra for the lithiated sample shows enhanced intensity in the low angle spectra near 107 eV, with respect to the nonlithiated SiC. At higher penetration conditions, the spectrum begins to closely resemble the EG/SiC and as-received SiC control samples. Based on the variation in X-ray penetration with incident angle, these results indicate that lithiation changes the Si chemical bonding in the top 2–8  $\mu\text{m}$  of the sample.

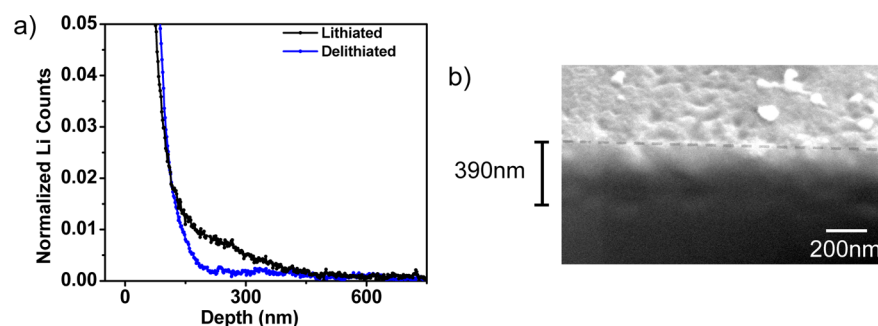
**4.3. Secondary Ion Mass Spectrometry and Cross-Sectional Scanning Electron Microscopy.** The initial stages of lithiation and delithiation in EG/SiC were explored via time-of-flight secondary ion mass spectrometry (SIMS) and cross-sectional scanning electron microscopy (SEM). Only about 1  $\mu\text{m}$  depth can be measured, because of the low sputtering rate and lack of long-term ion beam stability of the SIMS. Due to this limitation, the full Li profile could only be generated for lightly lithiated samples. Elemental depth profiles measured with SIMS are shown in Figure 5a,b for 0.074 mAh  $\text{cm}^{-2}$  lithiated graphitized SiC (which is more than 2 orders of magnitude less lithiated than the samples used for EELS and IXS) and as-received SiC lithiated to 0 V. The Li distribution extends deeper within the sample than either oxygen or fluorine, indicating that lithium extends into the SiC and is not associated with the formation of a SEI layer. The as-received SiC in contrast shows no penetration of Li, F, or O deeper than approximately 10 nm into the sample, although Li, F, and O are present on the surface of the sample as part of the SEI. The lack of Li in the bulk of the as-received SiC despite the presence of Li in the surface SEI layer demonstrates that the 5 kV Ga ions used for SIMS sputtering do not significantly drive Li ions into the sample by forward scattering.

Figure 5c,d shows FIB-prepared cross-sectional SEM images of the same samples measured in Figure 5a,b. In particular, Figure 5c reveals that the 0.074 mAh  $\text{cm}^{-2}$  lithiated EG/SiC sample possesses a brighter and inhomogeneous region within 150 nm of the surface, which can be associated with the SEI. More significantly, the region between 150 and 390 nm below the surface continues to show SEM contrast (albeit with reduced brightness compared to the SEI), which corresponds to the depth where lithium was detected with SIMS. On the other hand, the cross-sectional SEM image for lithiated as-received SiC (Figure 5d) shows only a thin layer that is less than 40 nm in thickness, again in agreement with the SIMS results.

The reversibility of the lithiation process was also explored with SIMS. Specifically, the sample lithiated to 0.074 mAh  $\text{cm}^{-2}$



**Figure 5.** Depth resolved secondary ion mass spectrometry (SIMS) for (a) a graphitized SiC sample lithiated with 0.074 mAh cm<sup>-2</sup> of charge and (b) an as-received SiC sample lithiated to 0 V. SIMS depth profiles were normalized by setting the maximum for each element to 1. (c and d) Focused ion beam (FIB) milled cross-sectional scanning electron microscopy (SEM) images of the samples in panels a and b, respectively. Dashed lines indicate the boundary in the images of the surface and the cross-sectional image below the surface (above and below the dashed line, respectively).



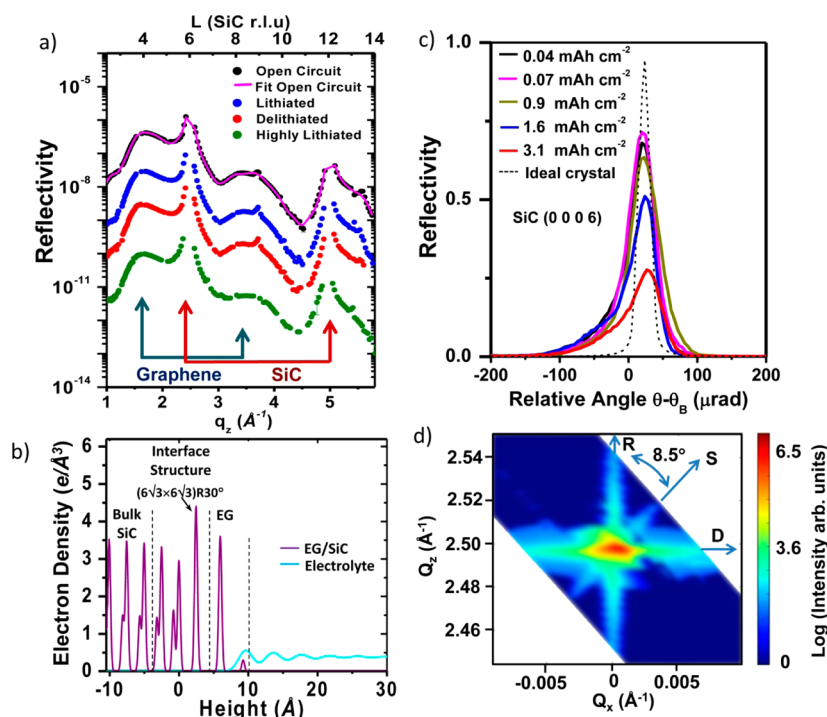
**Figure 6.** (a) SIMS depth profile of a 0.074 mAh cm<sup>-2</sup> lithiated graphitized SiC wafer and a portion of that wafer which was delithiated by 0.037 mAh cm<sup>-2</sup>. The lithium counts were normalized such that their maximum concentrations are 1, and the lithiated curve was shifted to the right by 21 nm to match the point where the F counts drop by 2 orders of magnitude. (b) Cross-sectional SEM of the delithiated sample. The surface and cross sectional images are shown above and below the dashed line, as in Figure 4.

was split into two pieces. One half of this sample was then delithiated by 0.037 mAh cm<sup>-2</sup>. SIMS measurements of the Li depth profiles for the two samples were then compared (Figure 6a). The lithiated curve is shifted in depth by 21 nm to account for the increased SEI thickness in the delithiated sample (see the Supporting Information, Figure S3). Following this shifting procedure, a substantial drop of Li is observed in the delithiated sample between 170 and 400 nm in depth, thus indicating that the lithiation reaction is at least partially reversible for the first few hundred nanometers of SiC. The cross-sectional SEM images in Figures 5c and 6b show that upon delithiation the region underneath the SEI darkens, which is consistent with the reduction in lithium concentration observed in the SIMS measurements.

## 5. X-RAY REFLECTIVITY

In situ X-ray reflectivity (XRR) measurements were performed to gain additional information about the structure of the SiC,

surface reconstruction, and graphene layers following lithiation. The in situ XRR results show that the EG/SiC interfacial structure is similar to that measured in air<sup>42</sup> when the EG/SiC is placed in the electrolyte at open circuit voltage. In situ XRR measurements were also performed during the lithiation and delithiation processes. Reflectivity curves at different states of lithiation are shown in Figure 7a. The XRR signal between the bulk SiC (000L) Bragg peaks for the in situ sample in Figure 7a show that the interfacial structure of the EG/SiC is not noticeably altered by lithiation. XRR data for a graphitized SiC sample at a highly lithiated state ( $\sim 14$  mAh cm<sup>-2</sup>, more than 2 orders of magnitude greater than the in situ data) were also collected to observe if there is any substantial structural change in graphene or SiC at high lithiation dose. There are only small changes in the XRR indicating that the graphene surface layer is not substantially modified and the majority of the SiC structure remains intact at this lithiation state. Figure 7b shows the extracted electron density of a nonlithiated graphitized silicon



**Figure 7.** (a) In situ X-ray reflectivity of graphitized SiC sample in the electrolyte at open circuit voltage, after lithiation ( $0.074 \text{ mAh cm}^{-2}$ ), after delithiation ( $0.037 \text{ mAh cm}^{-2}$ ), and a different graphitized SiC sample after  $14 \text{ mAh cm}^{-2}$  lithiation, offset vertically for clarity. The line is the best fit for the reflectivity data at open circuit voltage from which the electron density profile is determined. (b) Derived interfacial electron density profile measured at the open circuit voltage. (c) Absolute reflectivity data at SiC (0006) Bragg peak at different lithiation doses. ( $\theta_B$  is the Bragg angle for SiC (0006)). Also shown is the SiC (0006) reflectivity predicted by dynamical diffraction theory for an ideal perfect crystal. (d) 2D reciprocal space map near the SiC (0006) Bragg reflection for  $3.7 \text{ mAh cm}^{-2}$  lithiated EG/SiC. “R”, “S”, and “D” indicate the surface CTR reflectivity, lithiation-induced streak, and bulk SiC diffuse scattering, respectively.

carbide (EG/SiC), at open circuit voltage, using a model based least-squares fit analysis to the XRR data. The calculated reflectivity profile (solid line) in Figure 7a is the best fit from which the electron density profile (Figure 7b) is determined. The result shows a high degree of graphene single layer coverage ( $\sim 87\%$ ) with some bilayer coverage ( $\sim 7\%$ ). There is evidence of the  $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$  reconstruction layer at the interface and a SiC surface with structural and stoichiometric modifications within the top two bilayers. This resultant structure may be due to structural relaxations that arise during growth.<sup>42,51</sup>

While the surface structure of the SiC does not change significantly during lithiation, we find that the measured reflectivity of 6H-SiC (0006) bulk Bragg peak drops with lithiation dose, as shown in Figure 6c. Such a measurement is extremely sensitive to the perfection of the SiC bulk crystal within the dynamical diffraction X-ray extinction depth of  $1 \mu\text{m}$  into the SiC, at the 6H-SiC (0006) Bragg peak. The Bragg peak shows little changes until the lithiation dose exceeds  $1 \text{ mAh cm}^{-2}$  and then the (0006) Bragg peak intensity decreases by a factor of  $\sim 2.5$  at  $3.1 \text{ mAh cm}^{-2}$  of lithiation. Due to limitations in time available for these in situ experiments at the synchrotron, no higher lithiation states could be measured. No substantial amount of attenuation is expected at the SiC (0006) Bragg peak due to SEI formation in these measurements with a photon energy of  $17 \text{ keV}$ . Hence, the change of peak intensity and shape is attributed to a decrease in bulk SiC crystallinity due to Li incorporation into the system.

During the in situ lithiation process, the emergence of a new streak in the 2D reciprocal space map (RSM) (shown as “S” in Figure 7d) was observed near the SiC (0006) Bragg reflection.

The intensity of this streak grows with increasing lithiation dose, suggesting that it is directly associated with the lithiation process. Such streaks in reciprocal space, penetrating through the (0006) SiC Bragg peak, are associated with the development of interfacial planes (such as surfaces and grain boundaries) in the SiC lattice and are oriented normal to the defect plane. This observation suggests that planar defects play a role in the lithiation process of SiC. This streak is tilted by an angle of  $\sim 8.5^\circ$  with respect to the surface crystal truncation rod (CTR) in this two-dimensional projection image of the RSM. From inspection of the full 3D RSM, the upper bound for the tilt of the planar defect orientation with respect to the SiC surface plane is approximately  $10^\circ$ . The specific orientation of this streak could not be assigned to any known grain boundary structures in SiC. This new defect structure could be explained by a number of phenomena including faceting, grain boundaries, or the development of a plane with increased Li concentration.<sup>52–54</sup> The lithiation process may create these defects, or the Li may interact with defects that are already present (e.g., created by thermal annealing), thereby making the streaks more visible in the RSM. Since the EELS and IXS measurements suggest a Li stoichiometry as high as 1:1, it is apparent that the lithiation of this defect structure cannot fully explain the bulk stoichiometry. It does, however, provide a potential mechanism for the penetration of lithium into the bulk SiC that does not rely entirely on bulk site diffusion.

## 6. DISCUSSION

In this study, we have observed over an order of magnitude enhancement of the first lithiation capacity of doped SiC via

high temperature processing. TEM and EELS results show that the lithium stoichiometry has an approximately 1:1 ratio with Si within at least the top 3  $\mu\text{m}$  of the SiC surface. IXS and SIMS further confirm that the lithium extends further into the bulk than F and O species that are associated with the SEI layer. The XRR results show that there is little change to the graphene layers upon lithiation, consistent with the HRTEM results. Unlike Si, which amorphizes starting at the surface during lithiation,<sup>55</sup> the EG/SiC surface remains intact. However, there is a substantial drop in the SiC (0006) Bragg peak intensity, which indicates some change to the bulk SiC crystallinity, which is likely due to the development of defects. Also, IXS data show a change in the Si near-edge structure, which can be explained by changes to the Si environment, mostly likely due to its interaction with Li. We therefore conclude that Li penetrates into the bulk of SiC upon electrochemical lithiation of doped EG/SiC.

Several factors may contribute to the enhanced lithiation of doped EG/SiC compared to as-received SiC. For example, sufficient electrical conductivity of the surface and substrate are necessary to allow for electron transfer. This combination can be achieved in doped SiC following removal of the native oxide via high temperature vacuum annealing. In particular, vacuum annealing to the point of epitaxial graphene formation results in an electrically conductive, chemically passivated surface that provides long-term protection against surface oxidation and thus appears to be the most relevant and promising for long-term electrochemical studies and applications. The carbon-rich subsurface reconstruction and/or the development of defects in the bulk crystal during high temperature processing may also facilitate Li diffusion in SiC. From the TEM and XRR results, it is apparent that Li penetrates deep into the crystal without substantial changes in lattice constant. While the RSM suggests that defects may facilitate Li diffusion and provide sites for Li incorporation, the high Li:Si stoichiometry obtained by EELS and IXS suggests that incorporation at defects is insufficient to explain the observed stoichiometry and that Li also resides in the bulk crystal lattice. It is also possible that regions of the SiC are amorphizing to accommodate Li. If such regions exist, they would likely need to be on the order of a few nanometers in size, such that the approximately 100 nm thick TEM samples would appear relatively uniform. To explain the stoichiometry, approximately 20% of the crystal would need to amorphize, assuming ideal Li capacity for the amorphized Si atoms. While some small variations in the TEM images are observed in the SiC crystalline regions, it is difficult to definitively attribute these variations to defects, amorphization, or issues of sample preparation.

## 7. CONCLUSIONS

In conclusion, we have shown that graphitization of doped SiC activates the inert SiC substrate for lithiation, thus enabling substantially increased lithium incorporation in the bulk crystal. EELS analysis shows that Li is present in a stoichiometry as high as  $\{1 \pm 0.2\}$ :1 ratio of Li to Si. This apparent stoichiometry corresponds to a Li-ion capacity of  $670 \pm 130$  mAh/g, which is approximately double that of the graphite anodes currently used in Li-ion batteries. This enhanced lithiation requires substantial electrical conductivity of the substrate and surface, which is enabled by doping and removal of the native oxide via graphitization, respectively. In this manner, this work has shown that a relatively straightforward surface treatment is sufficient to convert doped SiC from an

inactive, inert substrate into an electrochemically active host for Li. This ability to substantially enhance lithiation via surface modification highlights the importance of interfacial engineering as an alternative pathway for identifying and engineering materials for next generation Li-ion battery electrodes.

## ■ ASSOCIATED CONTENT

### Supporting Information

LEED images of EG/SiC and  $\sqrt{3} \times \sqrt{3}$  sample; details of SIMS, TEM and EELS measurements; TEM and EELS of C-face of lithiated EG/SiC. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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